XI. *Researches on Organo-metallic Bodies.*—Second Memoir. *Zincethyl.*
By E. FRANKLAND, *Ph.D., F.R.S.,*
Professor of Chemistry in Owens College, Manchester.

IN a former memoir on organic compounds containing metals*, after describing the preparation, composition, and properties of zincmethyl, I mentioned the corresponding formation of the homologous compounds zincethyl and zincamyl; but although the composition of these latter bodies was to a certain extent fixed, by the study of the products of their decomposition in contact with water, yet the difficulty of procuring them in sufficient quantity, by digesting the iodides of methyl, ethyl, and amyl, with zinc, in strong glass tubes at high temperatures, was so great, that I could neither extend their investigation further, nor succeed in rendering even the history of zincmethyl quite complete. In pursuance, however, of the intention announced in the memoir just alluded to, I subsequently commenced studying the action of these bodies upon certain organic compounds containing chlorine and other electro-negative elements, with a view to replace these elements by the groups $C_2 H_3$, $C_4 H_5$, &c., but meeting with some unexpected results, it appeared to me highly desirable, first to complete the history of at least one of the organo-zinc compounds, before proceeding further with the substitution experiments.

From the comparative facility with which the materials for the preparation of zincethyl can be procured, I selected this body as the subject of my experiments; and as it was necessary to prepare it in much larger quantities than heretofore, which could not be accomplished without great danger in sealed glass tubes heated in an oil-bath, I availed myself of the proximity of Mr. NASMYTH to get constructed two vessels of enormous strength, in which these operations might be conducted, on a tolerably large scale, without risk of dangerous explosions; and I take this opportunity of thanking that eminent engineer for the very kind and effectual manner in which he carried out my views with regard to these instruments, both of which are quite indispensable for the prosecution of researches with organo-metallic bodies in general, but especially with those containing zinc.

The one I will first describe is employed as a PAPIN's digester, and sealed glass tubes can be heated in it to any temperature below redness. It is constructed entirely of Low Moor wrought iron, and consists of a cylinder, A, A (fig. 1), closed

* Transactions of the Royal Society, 1852, p. 417.

at the bottom, and welded in one piece by the steam-hammer. This cylinder is $18\frac{1}{2}$ inches long, $\frac{5}{8}$ inch in thickness, and 3 inches internal diameter; it is furnished at top with a flanch, B, B, $1\frac{3}{8}$ inch broad and $\frac{5}{8}$ inch thick, its upper surface turned true, and having an internal annulus sunk $\frac{1}{20}$ inch below the level of the surrounding surface. The cap of the digester, C, C, is made to fit upon this flanch, with which it corresponds in thickness and dia-meter; it is furnished with a projecting face $\frac{1}{4}$ inch deep, fitting the mouth of the cylinder exactly. Within the circle of this projecting face, the cap is perforated by two aper-tures, into one of which is securely fixed the cast-iron tube $d\,d$, closed at the bottom, 6 inches long and $\frac{1}{2}$ inch internal diameter, forming a mercury bath for the reception of a thermometer. The other aperture, which is bouched with brass, serves as the bed of the safety valve e, which con-sists of a piece of brass wire $\frac{1}{8}$ inch diameter, slightly flat-

Fig. 1.

tened on two sides and furnished with a head accurately ground to the surface of the cap: pressure is applied to this valve in the usual manner by the lever and weight f, g. Both the flanch and cap are perforated by four holes for the reception of four screw bolts $\frac{1}{2}$ inch in diameter, which are inserted from below, and work into nuts that can be tightly screwed up by a lever key. The whole of the pressure produced by these screw bolts is made to take effect exclusively upon the surface of a leaden washer $\frac{1}{8}$ inch thick, placed in the sunken annulus above mentioned; and thus the apparatus is made perfectly impervious to gases and vapours, even under the enormous pressure of more than 100 atmospheres. Before use, this vessel was proved, by being two-thirds filled with water, and then gradually heated up to the melting-point of lead. It has since been exposed with impunity to a still more severe test; for on one occasion, when charged with water and a glass tube filled with iodide of methyl, at a temperature of 200° C. the glass tube burst, and such was the tension of the iodide of methyl vapour, that the safety valve was instantaneously expelled, and the heavily loaded lever thrown completely over. In this digester, volatile liquids enclosed in glass tubes of large dimensions and moderate thickness of glass, may be exposed to any temperature below redness with safety. I prefer to use water in the digester, but other and less volatile liquids may of course be substituted if desired: in most expe-riments, however, it is important that the pressure upon the exterior of the glass tubes should not be much less than that in their interior, and this condition is generally secured by the employment of water in the apparatus.
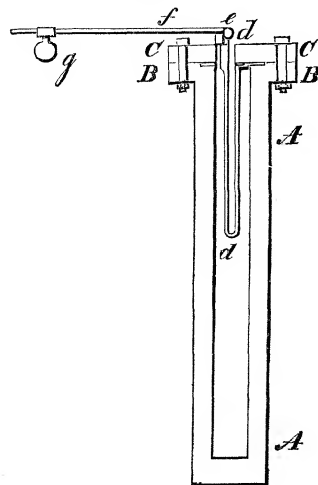
The second digester is made of wrought copper and is of smaller dimensions, being especially designed for the preparation of large quantities of organo-zinc compounds, without the intervention of glass tubes. It consists of a wrought copper tube, A, A (fig. 2), 18 inches long, $1\frac{1}{4}$ inch internal diameter, and $\frac{1}{2}$ inch in thickness, drawn

from a solid mass of the metal by a recently invented process. This tube is closed at bottom by a screw plug, and is furnished at top with a brass flanch, B, B, $1\frac{5}{8}$ inch broad and 1 inch thick, screwed upon the copper tube: the vessel thus formed is closed by the brass cap C, C, of the same dimensions as the flanch upon which it fits. The cap is furnished with a central projection 1 inch deep, fitting the copper tube, and pierced with a central aperture D, tapped to receive the screw plug E, which, with the intervention of a collar of lead, effectually closes the aperture. The cap C C is secured to the digester by three screw bolts $\frac{1}{2}$ inch in diameter, which are inserted from above and screw into the lower flanch. Perfect impermeability to gases is secured, as in the iron digester, by a sunken annulus and a ring of lead. When it is desirable to collect the gases evolved during any operation in this digester, the plug E is replaced by a carefully made stopcock, to the nozzle of which a gas-delivery tube can be attached, when the reaction is completed. This digester is heated by means of a cylindrical copper oil-bath placed in a gas-stove, as shown in fig. 3. The gas-stove consists of a strong wrought-iron framework, A, A, around which is fixed the sheet-iron cylinder B, B closed at the bottom, but furnished with a draught regulator C, and contracted at top by a ring of sheet iron so as just to admit the cylindrical oil-bath D, D, the flanch of which rests upon the upper extremities of the wrought-iron framework, which are turned inwards for this purpose. The sheet-iron cylinder is surrounded by another of polished tin plate to prevent the too rapid radiation of heat; there is an interval of half an inch between the two cases, and both are pierced with holes at E for the exit of the products of combustion. A $\frac{1}{4}$-inch copper pipe, F, pierced with eighteen or twenty small apertures, forms the gas-burner. By this arrangement, it is easy to maintain an almost constant degree of heat for any length of time. The temperature is ascertained by the thermometer f, immersed in the oil-bath through an aperture bored in the cap and flanch of the digester for this purpose. This gas-stove is also used for heating the iron digester, but without the intervention of the oil-bath. In this copper digester, which is capable of resisting enormous pressure, it is easy to prepare four or five ounces of zincethyl at one operation.

The zincethyl used in the experiments detailed below, was prepared in the following manner. The copper digester, well cleaned, dried, and heated to about 150° C.,
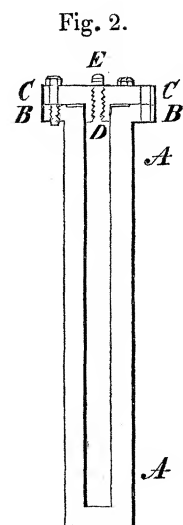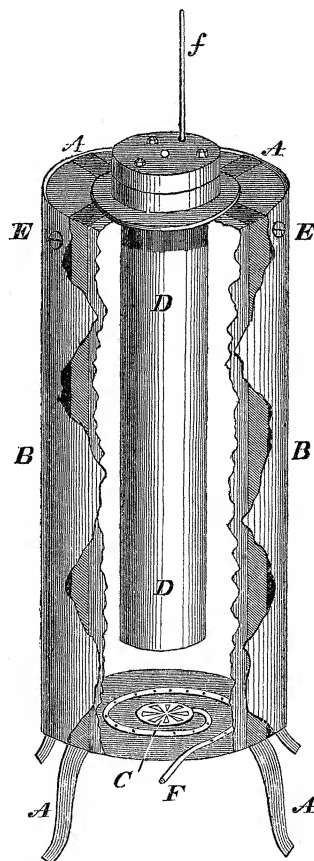
Fig. 2.

Fig. 3.

was charged with four ounces of finely granulated zinc, which had been previously heated to the same temperature, for at least half an hour, in order to get rid of every trace of moisture, the presence of which, in the ingredients used for the preparation of organo-zinc compounds, must be most carefully avoided, as all these compounds are instantaneously decomposed by contact with water into oxide of zinc and hydride of the organic radical: extraordinary care therefore, in freeing the materials perfectly from moisture, is amply repaid in the increased quantity of the product.   As soon as the hot zinc had been introduced into the digester and slightly rammed down, the cap C, C was securely screwed into its place, the plug E inserted, and the apparatus allowed to become cold.   Two ounces of iodide of ethyl, by measure, were then mixed with an equal bulk of ether*, which had been well washed and subsequently distilled several times from anhydrous carbonate of potash.   About 100 grains of anhydrous phosphoric acid were then added to this mixture, which was well agitated and allowed to stand for half an hour: the phosphoric acid gradually cohered into a porous gummy mass, from which the ethereal mixture could be readily decanted and poured into the digester through a funnel inserted in the aperture D.   The plug E being then firmly screwed down, the digester was placed in the oil-bath, and maintained at a temperature of about 130° C. for twelve or eighteen hours: at the end of this time traces only of iodide of ethyl remained undecomposed.

After the apparatus had been allowed to cool, the screw E was loosened, to allow a quantity of gas, principally hydride of ethyl, to escape; if all the materials were carefully freed from moisture, the quantity of gas was insignificant, but if moisture were present it was much larger, being derived, as above stated, from the decomposition of zincethyl.   When the gas had escaped, the screw was removed and replaced by a cork and bent tube, conveniently arranged for the distillation of the volatile contents of the digester.

As zincethyl is spontaneously inflammable in air and instantaneously decomposed by water, it is necessary that the vessels into which it is distilled should be kept constantly filled, either with dry hydrogen, nitrogen, or carbonic acid gas; the latter I have found most convenient in practice.   The maintenance of an atmosphere of this gas can be easily effected by the following arrangement of apparatus, fig. 4.   A is a WOULF's bottle for the generation of the carbonic acid, which streams through a chloride of calcium tube B, and WOULF's bottle C containing concentrated sulphuric acid, before entering the reservoir D, which should be of about two quarts' capacity, and contain a stratum of concentrated sulphuric acid about one inch deep.   From this reservoir the dry gas can be allowed to escape, either by the tube e into the vessel f, or through the retort g by the tube h.

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* I have already pointed out that the admixture of ether almost entirely prevents the elimination of gases during the reaction (Journ. Chem. Soc. vol. ii. pp. 293 and 298), and BRODIE (Journ. Chem. Soc. vol. iii. p. 409) has since shown that it greatly facilitates the production of zincethyl, nearly the whole of the iodide of ethyl being transformed into this body.

When all is prepared for the distillation of the zincethyl, the reservoir D being filled with carbonic acid, and the tube i from the digester (which latter still remains

Fig. 4.
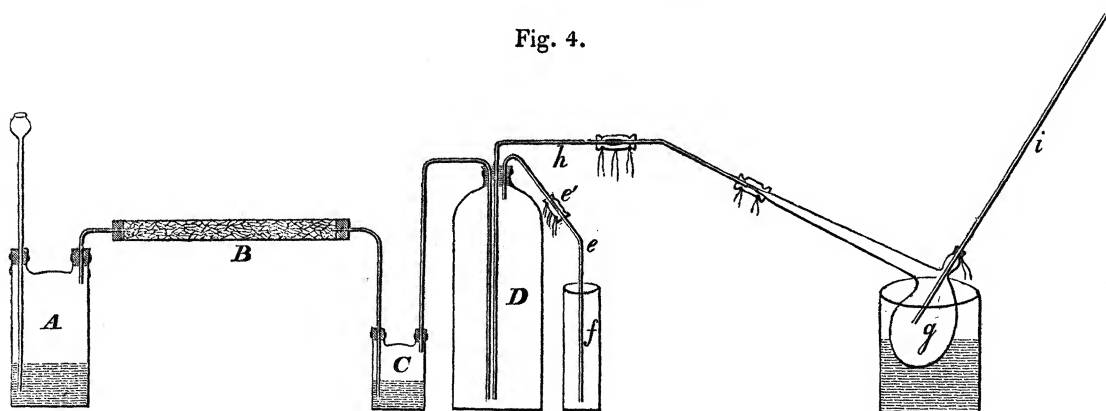
in the oil-bath and gas-stove) inserted into the tubulure of the retort g, the stream of carbonic acid, which has hitherto flowed through f, is cut off at e' by a caoutchouc valve, and is thus made to flow through g, making its escape between the tubulure and the tube i.   After the carbonic acid has taken this route for a sufficient length of time to ensure the complete expulsion of air from g, a piece of sheet caoutchouc is passed round the tubulure of g and the tube i, so as to make the union gas-tight, whilst at the same moment an assistant opens the caoutchouc valve e'; thus allowing the carbonic acid again to escape through f.   The retort g is thus connected with a reservoir kept constantly filled with pure and dry carbonic acid, which effectually excludes atmospheric oxygen and moisture from g during the distillation. Heat being now applied to the digester, by means of the gas-stove and oil-bath, ether begins to distil over, so soon as the temperature of the digester exceeds the boiling-point of that liquid.   The first half-ounce is nearly free from zincethyl and might be collected apart, but I generally prefer to receive the whole product of the distillation in one vessel.   As the temperature rises to 140° or 150° C. the product becomes more and more rich in zincethyl, but a heat of 190° C. is required to bring over the last portions of this body, a large quantity of which is apparently in some form of combination with the iodide of zinc, and can only be expelled at a very much higher temperature than the boiling-point of zincethyl.   During the last stages of the distillation, there is a slow evolution of gas, due to the decomposition of a small portion of the zincethyl by the high temperature required for its complete expulsion.

After the whole of the volatile products have passed over, the tube i must be carefully withdrawn from g and immediately replaced by a thermometer passing through a well-dried cork.   The beak of the retort, disconnected from the tube h, must now be inserted air-tight into a suitable tubulated receiver, previously filled with dry carbonic acid, the tubulure of which is connected with the carbonic acid receiver D, and the rectification may now be commenced.   The liquid begins to boil at

about 60° C., but the thermometer gradually rises until about three-fourths have passed over, when it becomes stationary at 118° C. The receiver must now be changed, the retort being first allowed to become quite cold. On the subsequent application of heat, the whole of the remaining liquid distils over at 118° C. This is pure zincethyl, and may be received in a peculiarly constructed vessel, from which it can be conveniently expelled in small quantities as required.

This vessel, which is a kind of syringe glass, is repre-

Fig. 5.

sented by fig. 5. A, A is a tall glass cylinder with a slightly contracted mouth, well fitted with a sound and thoroughly dry cork coated with gutta percha varnish. Through this cork pass three tubes: one a, terminates just below the cork and projects about 2 inches above the mouth of the cylinder; it is about a quarter of an inch internal diameter, and serves to receive the drawn-out beak of the retort g (fig. 4) during the distillation of the pure zincethyl: when the distillation is completed, a is closed by a cork covered with sealing-wax. Another tube, b, one-sixteenth of an inch bore, passes to the bottom of A; it is bent above at an acute angle, and, after passing through a small cork d, terminates at c in a capillary orifice. The cork d serves to close another small tube, e, which encases b, and protects its capillary orifice from the atmosphere. The third tube, f, connects the upper part of A, A with a chloride of calcium tube g, g, to the opposite extremity of which the thin caoutchouc globe h is attached. By removing the tubular cap e and pressing h, which is previously filled with carbonic acid, it is thus easy to transfer any required quantity of the liquid in A to any other vessel.
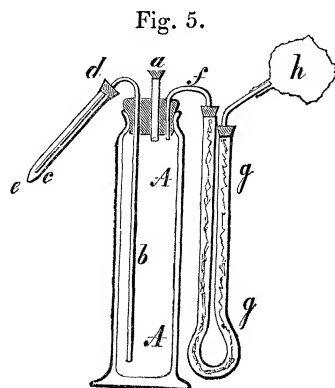
To determine the composition of zincethyl, a quantity was transferred into a small glass bulb with a very narrow mouth, previously filled with dry carbonic acid. A number of smaller glass bulbs, capable of containing about 5 decigrammes of the liquid and having long capillary tubes attached, were then filled with carbonic acid by being repeatedly heated and cooled in an atmosphere of this gas; these bulbs were then partially filled in the usual manner with zincethyl from the larger bulb above mentioned, and the increase of weight being noted, they served for the following quantitative determinations:—

I. ·2578 grm., burnt with oxide of copper and oxygen, gave ·3653 grm. carbonic acid and ·1915 grm. water.

II. ·2443 grm., similarly treated, gave ·3495 grm. carbonic acid and ·1799 grm. water.

III. ·3139 grm., slowly decomposed in a graduated tube filled with slightly acidulated water, gave ·2045 grm. oxide of zinc and ·1459 grm. hydride of ethyl, as deduced from the annexed observations:—

	Observed volume.	Height of inner column of water.	Temperature.	Height of barometer.	Corrected volume at 0° C. and 760 mm pressure.
Volume of Hydride of Ethyl	cub. cent. 113·38	mm 178·5	15·0° C.	mm 766·0	cub. cent. 108·23

These determinations agree with the formula

$$C_4 H_5 Zn,$$
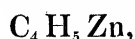
as is seen from the following comparison :—

	Calculated.		Found.			
			I.	II.	III.	Mean.
C_4	24·00	39·01	38·64	39·02	44·93	38·83
H_5	5·00	8·13	8·25	8·15		8·20
Zn	32·52	52·86	——	——	52·27	52·27
	61·52	100·00			97·20	99·30

In experiment No. III. the volume of hydride of ethyl is considerably less than that required by the above formula, owing no doubt to its solubility in the acidulated water used as the confining fluid; in fact a similar error, to a less extent, occurred in the corresponding experiment with zincmethyl*; but to place the cause of error beyond all doubt, the following additional determination was made. Into a graduated eudiometer tube, filled with mercury, an indefinite quantity of zincethyl, enclosed in a glass bulb, was introduced, the capillary stem of the bulb being broken inside the eudiometer tube. A few drops of water were now passed up into the same tube, and the apparatus was exposed to a heat gradually raised to the boiling-point of zincethyl, the conversion of which into hydride of ethyl and oxide of zinc was thus perfectly effected, whilst a few drops of water only exerted an absorptive action upon the former. After the apparatus had again become cold, the following observations were made :—

	Observed volume.	Temperature.	Difference of mercury level.	Height of barometer.	Corrected volume at 0° C. and 760 mm pressure.
Volume of Hydride of Ethyl	cub. cent. 114·62	13·5 C.	mm 135·0	mm 763·2	cub. cent. 88·61

The oxide of zinc, carefully dissolved from the interior of the eudiometer and from the mercury, by dilute hydrochloric acid, re-precipitated as basic carbonate and then ignited, weighed ·1603 grm.

These numbers correspond almost exactly with those which ought to be obtained from zincethyl :—

* Philosophical Transactions, 1852, p. 431.

	Calculated.		Found.
C_4H_5 . . .	29·00	47·14	47·33
Zn	32·52	52·86	52·67
	61·52	100·00	100·00

At ordinary temperatures zincethyl is a colourless, transparent, and mobile liquid, refracting light strongly and possessing a peculiar odour, rather pleasant than otherwise, and therefore differing greatly from that of zincmethyl. Its specific gravity is 1·182 at 18° C. Exposed to a cold of −22° C., it exhibited no tendency to become solid. Zincethyl boils at 118° C., and distils unchanged. The specific gravity of its vapour is 4·259, according to the following determination by GAY-LUSSAC's method:—

Weight of zincethyl used	·3103 grm.
Observed volume of vapour	106·0 cub. cent.
Temperature	148° C.
Height of inner column of mercury	129·0 mm.
Height of barometer	764·8 mm.
Volume of residual gas* at 0° C. and 760 mm pressure . . .	2·78 cub. cent.
Corrected volume of vapour at 0° C. and 760 mm pressure .	56·07 cub. cent.
Specific gravity of vapour	4·259

Zincethyl vapour, therefore, consists of one equivalent of zinc vapour and one volume of ethyl gas, the two being condensed to one volume:—

1 volume of ethyl gas	2·0039
1 equivalent of zinc vapour	2·2471
1 volume of zincethyl vapour . . .	4·2510
Found by experiment	4·259

This vapour volume of zincethyl is highly remarkable, and almost compels us to conclude, that the vapour volume of the double atom of zinc is only equal to that of oxygen, instead of corresponding with the volume of hydrogen, in accordance with the generally received supposition. Zincethyl, therefore, appears to belong to the so-called water type, and to consist of two volumes of ethyl and one volume of zinc vapour, the three volumes being condensed to two: for if we were to assume that an equivalent of zinc occupies the same vapour volume as an equivalent of hydrogen, we

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* This residual gas consisted of hydride of ethyl derived from the decomposition of a portion of the zincethyl by traces of moisture adhering to the tube or mercury, the total removal of which appears to be impossible. The space occupied by this hydride of ethyl would obviously be exactly double that occupied by the zincethyl, from which it was derived. The observed and corrected volume of zincethyl vapour (57·46 cub. cent.) was consequently too great by $\frac{2·78}{2} = 1·39$ cub. cent., and hence the true volume of ·3103 grm. of zincethyl vapour was, as above stated, 56·07 cub. cent.

should then have the anomaly of the combination of equal volumes of two radicals being attended by condensation. The determination of the specific gravity of zinc-ethyl vapour supplies us with the first datum respecting the vapour volumes of the class of metals to which zinc belongs. It has hitherto been assumed, that the vapour volume of these metals is equal to that of hydrogen; but the vapour volume of zinc-ethyl goes far to contradict this assumption.

Although zincethyl is remarkable for the intense energy of its affinities, which place it nearly at the head of the list of electro-positive bodies, yet it does not appear to be capable of forming any true compounds with electro-negative elements, its reactions being all double decompositions in which the constituents of the zincethyl separate. When a few drops of zincethyl, diluted with ether to prevent inflammation, are passed into a mercurial eudiometer containing dry atmospheric air, a rapid absorption of oxygen takes place, with the formation of a white amorphous solid composed of zinc, ethyl, and oxygen. This reaction, which is also common to zincmethyl and zincamyl, led me to suppose, that, like cacodyl, these bodies combined directly with oxygen*; but the results of the action of oxygen upon zincethyl detailed below, prove that no such compound is formed; the white body being ethylate of zinc, and not an organo-metallic compound, in the strict sense of the term.

Action of Oxygen upon Zincethyl.

When zincethyl is brought into contact with oxygen or atmospheric air, it instantly ignites, burning with a brilliant blue flame, fringed with green, and evolving dense clouds of oxide of zinc; a cold body held in this flame, becomes coated with a black deposit of metallic zinc, surrounded by a white ring of oxide of zinc. In this rapid action of oxygen, all the elements of zincethyl are attacked, and the products are oxide of zinc, water, and carbonic acid; but if the zincethyl be placed in a vessel filled with dry carbonic acid and immersed in a freezing mixture, oxygen gas may be slowly admitted without inflammation taking place. At first the absorption of oxygen is rapid and attended with the production of white fumes, which fall to the bottom of the vessel in the form of a white powder; but the action soon becomes greatly retarded, owing to the formation of a solid crust upon the surface of the zincethyl, protecting the latter from further contact with oxygen, so that after the lapse of weeks, or even months, the oxidation is very imperfect. During the progress of the oxidation, a small quantity of a black substance, resembling finely-divided metallic zinc, is deposited from the liquid; but the amount of this deposit is so small, that I did not succeed in obtaining more positive evidence of its nature.

As this mode of oxidizing zincethyl in a pure state was found to be incapable of yielding results from which the nature of the action could be readily deduced, it was modified by mixing the zincethyl with about three times its bulk of anhydrous ether, and then submitting it, as before, to a slow current of oxygen. At first the absorp-

* Philosophical Transactions, 1852, p. 431.

tion of the gas took place rapidly, and was accompanied, as in the case of pure zinc-ethyl, with the formation of white fumes; these however soon ceased, and a white precipitate began to be deposited; but, by frequent agitation of the vessel, the formation of impervious crusts was prevented, and thus the oxidation, though slow, was continuous, and became complete in four days. During the latter part of the oxidizing process, and after the disappearance of the white fumes, a considerable quantity of inflammable gas, having the properties of hydride of ethyl, was evolved. When the oxidation appeared complete, the current of dry oxygen was replaced by one of atmospheric air, which was continued for two days longer, until the whole of the ether had volatilized. The solid product left in the flask was then transferred to a well-stoppered bottle placed in a closed receiver over sulphuric acid. It presented the appearance of a white porous amorphous substance, light and friable, possessing a very slight, but peculiar and agreeable ethereal odour. Heated in a close vessel it suffered no change until the temperature reached 90° C., when a sudden and almost explosive generation of volatile matters occurred, leaving a dirty yellow-coloured solid residue, which suffered no further change up to 150° C., but which, before attaining a red heat, evolved a considerable quantity of gas burning with a blue flame. Exposed *in vacuo* over sulphuric acid for twelve hours and then submitted to analysis, the product of oxidation yielded the following results :—

I. ·6285 grm., burnt with oxide of copper, gave ·5840 grm. carbonic acid and ·3027 grm. water.

II. 1·1257 grm. gave 1·0534 grm. carbonic acid and ·5363 grm. water.

III. ·9635 grm., treated with dilute hydrochloric acid, in which it dissolved, was precipitated boiling by carbonate of soda, and the precipitated basic carbonate of zinc washed, dried, and ignited : it yielded ·5040 grm. oxide of zinc.

IV. 1·1205 grm., cautiously ignited with access of air, gave ·5849 grm. oxide of zinc.

These results lead to the following per-centage numbers :—

	I.	II.	III.	IV.	Mean.
C	25·34	25·52	——	——	25·43
H	5·35	5·29	——	——	5·32
ZnO	——	——	52·58	52·20	52·39
O	——	——	——	——	16·86
					100·00

These figures correspond with no probable formula, and evidently denote the white product of the oxidation of zincethyl to be a mixture and not a pure substance. It is worthy of remark, however, that the relative atomic proportion of carbon and hydrogen is nearly the same as in ethyl :—

Analysis No. I.

Atoms of Carbon : atoms of Hydrogen = 4 : 5·06.

Analysis No. II.

Atoms of Carbon : atoms of Hydrogen $= 4 : 4\cdot98$.

As this substance is scarcely soluble in either ether or absolute alcohol, and is decomposed by water as well as by heat, there appeared no possibility of separating its proximate constituents, and I therefore sought for some further clue to its nature in the products of its decomposition. A preliminary experiment showed that water acted upon it energetically, the solid became transitorily coloured yellow, a peculiar odour was developed, similar to that produced when iodine is dissolved in a solution of a caustic alkali, and the water became impregnated with alcohol, for on being treated with acetate of potash and sulphuric acid, it gave the characteristic odour of acetic ether. After washing the solid residue of this reaction with a small quantity of water, and drying *in vacuo*, it yielded a mere trace of carbonic acid on ignition with oxide of copper, and was found to be pure oxide of zinc. This behaviour afforded strong evidence, that one of the chief constituents of oxidized zincethyl is ethylate of zinc,

$$ZnO\,C_4H_5O.$$
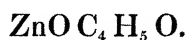
In order to ascertain more clearly the change which contact with water produced in the oxidized product, a portion of the same specimen, which yielded the above analytical results, was saturated with water and exposed over sulphuric acid *in vacuo* until it ceased to lose weight. Submitted to analysis it then yielded the following results :—

V. $\cdot6336$ grm., burnt with oxide of copper and oxygen, gave $\cdot1393$ grm. carbonic acid and $\cdot1412$ grm. water.

VI. $\cdot6678$ grm., cautiously ignited with access of air, gave $\cdot4766$ grm. oxide of zinc. These results agree with the formula
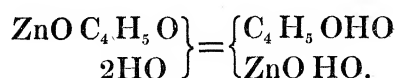
$$ZnO, HO, C_4H_3O_3 + 6ZnO\,HO,$$

as will be seen from the following comparison :

	Calculated.		Found.
C_4	24·00	6·04	5·99
H_{10}	10·00	2·51	2·48
$7ZnO$ . . .	283·64	71·33	71·37
O_{10}	80·00	20·12	20·16
	397·64	100·00	100·00

Although the occurrence of acetate of zinc and hydrated oxide of zinc in the above atomic proportions is probably only accidental, yet a comparison of these results with those of analyses Nos. I., II., III. and IV. prove that the action of water upon the oxidized product derived from zincethyl, consists in the replacement of ethyl by
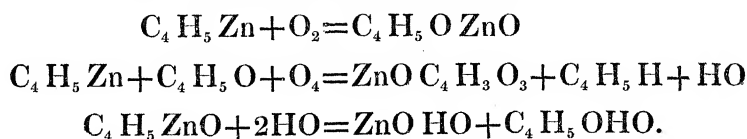
hydrogen or ether by water, and therefore confirms the conclusion drawn from its quantitative reactions, that it contains ethylate of zinc, which is no doubt decomposed by water in a manner quite analogous to the decomposition of the ethylates of potash and soda,

$$\left.\begin{array}{c} ZnO\ C_4H_5O \\ 2HO \end{array}\right\} = \left\{\begin{array}{l} C_4H_5\ OHO \\ ZnO\ HO. \end{array}\right.$$

When we consider the mode in which the oxidation of the zincethyl was effected, and the ease with which ether passes into acetic acid in the presence of free oxygen, there can scarcely be a doubt that the product of that oxidation consisted of a mixture of ethylate of zinc, acetate of zinc, and hydrate of zinc,

$$C_4H_5\ O\ ZnO$$

$$C_4H_3\ O_3\ ZnO$$

$$HO\ ZnO,$$
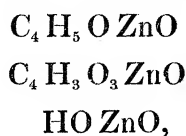
and that the following equations explain their formation, as well as that of hydride of ethyl, which was observed to escape during the latter stages of the oxidation :—

$$C_4H_5\ Zn + O_2 = C_4H_5\ O\ ZnO$$

$$C_4H_5\ Zn + C_4H_5\ O + O_4 = ZnO\ C_4H_3\ O_3 + C_4H_5\ H + HO$$

$$C_4H_5\ ZnO + 2HO = ZnO\ HO + C_4H_5\ OHO.$$

I conceive that the primary action of the oxygen is expressed by the first equation, and that this action alone goes on, so long as the vapours of zincethyl continue to diffuse themselves into the atmosphere of the flask in which the reaction takes place, and instantaneously absorb the oxygen as fast as it is admitted; but that so soon as that stage of the process is arrived at, where the zincethyl no longer forms vapour, which occurs when the white fumes cease, then the reaction expressed in the second equation commences, for it was proved, that from this time, free oxygen and ethyl vapour coexisted in the flask; but as it is difficult to conceive, that hydrated oxide of zinc can exist in the presence of zincethyl, it is probable that the reaction expressed by the third equation only occurs after the whole of the zincethyl has been oxidized.

Analyses Nos. I., II., III. and IV. indicate that the product of the oxidation of zincethyl has the following per-centage composition :—

|		
Ethylate of zinc	. . .	68·28
Acetate of zinc .	. . .	16·70
Hydrate of zinc	. . .	15·02
		100·00

The results of the separate analyses Nos. I., II., III. and IV. agree very nearly with

those which would be yielded by such a mixture, as is seen from the following comparison:—

	Calculated.	I.	II.	III.	IV.	Mean.
C . .	25·52	25·52	25·30	——	——	25·43
H . .	5·27	5·29	5·35	——	——	5·32
ZnO .	52·47	——	——	52·58	52·20	52·39
O . .	16·74	——	——	——	——	16·86
	100·00					100·00

Nevertheless, the behaviour of the body obtained by first saturating the oxidized product with water, and then drying over sulphuric acid *in vacuo*, convinces me that this body contains some other ingredient in addition to basic acetate of zinc; for on gradually heating it to 100° C., it exhaled a peculiar ethereal odour and became of a bright yellow colour; this ingredient is present, however, in small quantity only, and I have not succeeded in isolating it; possibly it is either aldehyde, or some product of the action of zincethyl upon acetic acid.

The most interesting reaction in the oxidation of zincethyl, and that to which I therefore directed my chief attention, is the formation of ethylate of zinc; not as regards the new compound of ether and zinc itself, but on account of the extraordinary *modus operandi* of the oxygen in its production. That ethyl, a body low down in the electro-positive series, should in this way unite with oxygen in the presence of a large excess of the intensely electro-positive zincethyl, is so remarkable and unexpected an occurrence, that such a view of the reaction could not be credited, unless supported by additional evidence more conclusive than that already advanced; especially as the formation of ethylate of zinc admits of an equally simple explanation on the supposition, that the ether it contains is derived from that employed to dilute the zincethyl, and that the carbohydrogen of the zincethyl is evolved either in its integral state, or transposed, as is usually the case, into hydride of ethyl and olefiant gas, thus—

$$C_4 H_5 Zn + O + C_4 H_5 O = C_4 H_5 O ZnO + C_4 H_5.$$
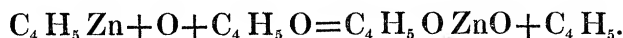
The oxidation of pure zincethyl would have decided this important question; but as it is impossible to obtain a perfect oxidation of pure zincethyl, this method could not be adopted. A solution of zincethyl in benzole would probably have united the requisite conditions for a successful experiment; but as I had no pure benzole at my command, and as the corresponding reactions of iodine, bromine and sulphur upon zincethyl furnish the key to this action of oxygen, I did not prosecute the inquiry further in this direction.

Action of Iodine upon Zincethyl.

Iodine acts upon zincethyl with great energy, and even with the evolution of heat and light, if a few grains of each be suddenly brought into contact. The violence of the action may, however, be conveniently moderated to any desired extent by the

intervention of ether, in which either ingredient, or both of them, may be dissolved. If the iodine and ether be perfectly anhydrous, and the solution of zincethyl in ether cooled below 0° C., the action is unattended by the evolution of any gas ; but if the temperature be allowed to rise above 10° C., a small amount of gas is given off near the close of the operation. To ascertain the nature of this reaction, a quantity of zincethyl, dissolved in the ether which had distilled with it from the copper digester, was placed in a flask and cooled to −20° C. A saturated solution of iodine in ether, both carefully freed from moisture, was then cautiously added in small quantities at a time, and with constant agitation of the contents of the flask, care being taken that the temperature never rose above 0° C. The addition of the iodine solution was continued until the intensity of the action had so far moderated as to allow of the iodine being used in the solid state, and it was then added in fine powder until the slight coloration of the liquor indicated that this element was present in excess and the action completed. The ethereal liquid remained transparent during the whole operation, and no gas was evolved. The completion of the reaction was also indicated by the solution of zincethyl ceasing to effervesce when a drop of it was brought in contact with water.

One portion of the solution thus saturated with iodine was allowed to evaporate spontaneously over sulphuric acid *in vacuo*. A white crystalline residue remained, and the sulphuric acid became filled with minute crystals of iodine, whilst on opening the receiver it evidently contained the vapour of iodide of ethyl. After exposing the white crystalline residue to a slow current of dry air for some hours, to remove the remaining traces of iodide of ethyl, it was ignited with oxide of copper, when it yielded traces only of carbonic acid and water ; it was in fact pure iodide of zinc. The second portion of the solution was distilled from a water-bath ; the distillate consisted of ether and iodide of ethyl ; on being frequently washed with water, dried over chloride of calcium and redistilled, it yielded a large quantity of pure iodide of ethyl, which boiled at 72° C., and gave the following analytical results :—

·7253 grm., burnt with oxide of copper, gave ·4155 grm. carbonic acid and ·2093 grm. water. These numbers correspond with the formula

$$C_4 H_5 I.$$

	Calculated.		Found.
C_4 . . .	24·00	15·40	15·61
H_5 . . .	5·00	3·21	3·21
I	126·88	81·39	——
	155·88	100·00	

The action of iodine upon zincethyl may therefore be expressed by the following equation :—

$$\left. \begin{array}{c} C_4 H_5 Zn \\ I I \end{array} \right\} = \left\{ \begin{array}{c} C_4 H_5 I \\ Zn I. \end{array} \right.$$
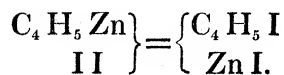
This result completely establishes the interpretation given above of the action of oxygen upon zincethyl, so far as regards the production of ethylate of zinc; but as a further confirmation, I ascertained the actual amount of iodine which was required for the complete decomposition of a certain quantity of zincethyl. The weight of the latter could only be ascertained approximatively by determining the weight of the iodide of ethyl from which it was derived. Taking this maximum weight as the basis of calculation, and assuming that every trace of iodide of ethyl had been converted into zincethyl, and the latter brought into contact with the iodine without any loss, then each atom of zincethyl took up 1·8 atom of iodine, a number which evidently confirms the above equation, when we take into account the numerous sources of loss of zincethyl incidental to the operations through which it passed.
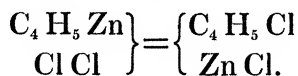
Action of Bromine upon Zincethyl.

The action of bromine upon zincethyl is exceedingly violent, and attended by dangerous explosions even when an ethereal solution of bromine is added to a dilute ethereal solution of zincethyl cooled to −15° C.; but the reaction can be conveniently effected by suspending a tube containing bromine in a flask half-filled with a solution of zincethyl in ether. The bromine vapour is gradually absorbed by the zincethyl solution until the latter is saturated. The products of the reaction are bromide of ethyl and bromide of zinc, and are therefore perfectly analogous to those yielded by the action of iodine upon zincethyl:

$$\left.\begin{array}{c} C_4\,H_5\,Zn \\ Br\,Br \end{array}\right\} = \left\{\begin{array}{c} C_4\,H_5\,Br \\ Zn\,Br \end{array}\right.$$
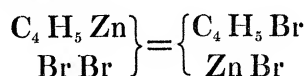
Action of Chlorine upon Zincethyl.

Zincethyl burns spontaneously with a lurid flame in an atmosphere of chlorine gas; the zinc and hydrogen are converted into chlorides, whilst carbon is deposited in the form of soot. I have not studied the products of a more moderate action, as it is difficult to bring the materials together without too great an elevation of temperature. There can be no doubt, however, that the moderated action of chlorine would be analogous to that of bromine, and that the products would be chloride of ethyl and chloride of zinc—

$$\left.\begin{array}{c} C_4\,H_5\,Zn \\ Cl\,Cl \end{array}\right\} = \left\{\begin{array}{c} C_4\,H_5\,Cl \\ Zn\,Cl. \end{array}\right.$$
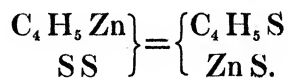
Action of Sulphur upon Zincethyl.

Carefully dried flowers of sulphur have only a slight action upon an ethereal solution of zincethyl, but the application of a gentle heat suffices to produce a brisk reaction; the sulphur gradually disappears, a white flocculent precipitate is formed, and a strong odour of sulphide of ethyl is developed. The chief product of this re-

action is the double sulphide of ethyl and zinc (mercaptide of zinc), which is produced as follows:

$$\left.\begin{array}{l} C_4 H_5 Zn \\ S\ S \end{array}\right\} = C_4 H_5 S + Zn\, S.$$
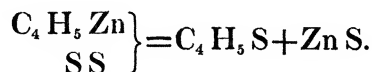
There is also formed a little free sulphide of ethyl, according to the following equation:

$$\left.\begin{array}{l} C_4 H_5 Zn \\ S\ S \end{array}\right\} = \left\{\begin{array}{l} C_4 H_5 S \\ Zn\, S. \end{array}\right.$$

The action of sulphur upon zincethyl is strikingly seen, if vulcanized india-rubber joints be used in the apparatus for the preparation of zincethyl; such joints, even when exposed only to the diffused vapour of zincethyl, soon become covered with pustules, which swell up to a large size and burst with slight explosions, until the caoutchouc is completely disintegrated.

This remarkable behaviour of zincethyl in contact with the electro-negative elements, cannot fail to have an important influence upon our views of the condition of bodies at the moment of chemical change,—a subject so ably discussed by BRODIE *, whose ingenious views, I consider, receive a new support from the reactions detailed in the foregoing pages. This behaviour also strikingly confirms the suggestions I ventured to make in a former memoir †, relative to the moleculo-symmetrical form of the organo-metallic compounds. In the inorganic combinations of zinc this metal unites with one atom only of other elements, a very instable peroxide, not hitherto isolated, being the only exception. The atom of zinc appears therefore to have only one point of attraction, and hence, notwithstanding the intense affinities of its compound with ethyl, any union with a second body is necessarily attended by the expulsion of the ethyl.

Action of Water upon Zincethyl.

I have already mentioned ‡ that water and zincethyl suffer mutual, and almost instantaneous decomposition, when brought into contact with each other, being transposed into oxide of zinc and hydride of ethyl,

$$\left.\begin{array}{l} C_4 H_5 Zn \\ HO \end{array}\right\} = \left\{\begin{array}{l} C_4 H_5 H \\ ZnO. \end{array}\right.$$
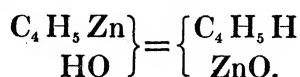
I have, in fact, already made use of this reaction as a means of analysing zincethyl, and it is therefore only necessary for me here to prove the composition of the gas evolved. For this purpose, a quantity of zincethyl was gradually decomposed by water, and the gaseous product collected. It had all the physical and chemical properties of the hydride of ethyl I have already described §, and yielded the following analytical results:

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* Philosophical Transactions, 1850, p. 789.   † Ibid. 1852, p. 438.
‡ Philosophical Transactions, 1852, p. 436.   § Journ. of Chem. Soc. vol. ii. p. 288; vol. iii. p. 341.

I. Fuming sulphuric acid did not reduce the volume of the gas.

II. Pressure of gas used . . . . . .   31·04

Pressure after admission of oxygen .   346·80

Pressure after combustion . . . .   268·92

Pressure after absorption of CO_2 . .   207·11

These numbers agree very nearly with those yielded by the combustion of pure hydride of ethyl, one volume of which consumes 3·5 volumes of oxygen and generates two volumes of carbonic acid.

Vol. of combustible gas.		Vol. of oxygen consumed.		Vol. of carbonic acid generated.
31·04	:	108·65	:	61·81
1	:	3·5003	:	1·991.

Zincethyl is similarly decomposed by the hydrated acids and by the hydrogen compounds of chlorine, bromine, iodine, fluorine and sulphur.

I cannot close this memoir without thanking my late assistant, Mr. C. J. TUFFNELL, for the aid he rendered me in several of the determinations mentioned above; his extreme accuracy and delicacy of manipulation enabled him to afford me very valuable assistance.